

Relation between the two-body entropy and the relaxation time in supercooled water

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The two-body excess entropy of supercooled water is calculated from the radial distribution functions obtained from computer simulation of the TIP4P model for different densities upon supercooling. This quantity is considered in connection with the relaxation time of the self intermediate scattering function. The relaxation time shows a mode coupling theory (MCT) behavior in the region of mild supercooling and a strong behavior in the deep supercooled region. We find here that the two-body entropy is connected to the relaxation time and shows a logarithmic behavior with an apparent asymptotic divergence at the mode coupling crossover temperature. There is also evidence of a change in behavior of the two-body entropy upon crossing from the fragile (hopping-free) state to the strong (hopping-dominated) state of supercooled water, and the relation that connects the two-body entropy and the relaxation time in the MCT region no longer holds.

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I. INTRODUCTION

The connection between dynamical properties and thermodynamics is an issue of particular interest in the study of supercooled liquids approaching the glass transition. However, a theoretical formulation able to address the problem of predicting the dynamical behavior from the thermodynamic properties is still missing. The dynamics of atoms in liquids is strongly connected to the local density fluctuations. The diffusivity is driven by the structural relaxation of the nearest-neighbor cages of atoms and the rate of structural relaxation is related to the number and distributions of the accessible configurations, so it is conceivable that the diffusivity and, more generally, transport properties can be related to the entropy.

The link between thermodynamics and transport properties is of particular interest in the study of the anomalous behavior of water in its supercooled liquid region. If it is possible to maintain water in the liquid state below its freezing point, supercooled water shows a strong increase in thermodynamic functions, like the isothermal compressibility, the isobaric specific heat, and the sound velocity. Extrapolations of these quantities show a possible divergence in a region below the line of homogeneous nucleation where liquid water is experimentally hardly kept in the liquid phase. This makes interpretation of the phenomenology rather difficult [1,2].

Computer simulations performed on different water models explain the anomalies of supercooled water with the presence of the coexistence between a low-density liquid and a high-density liquid terminating in a liquid-liquid critical point (LLCP). This interpretation is at the heart of a vivid debate in the literature [1,3–15].

Studies of the dynamical density correlators of water in computer simulations [16,17] found that the behavior upon supercooling can be interpreted in the region of mild supercooling in terms of the mode coupling theory (MCT) of the evolution of glassy dynamics [18]. According to the Angell phenomenological classification [19] this implies that water is a fragile liquid in this region. It was also found with

the use of different water models that, in approaching the region of the LLCP, there is a crossover from a fragile to a strong behavior in the structural relaxation of water [9,20–24] and confined water [25–27], in which this phenomenon was recently observed in experiments [28–32]. The locus of the fragile-to-strong crossover (FSC) is related to the line of maxima of the specific heat, which, close to the LLCP, can be identified as the Widom line emanating from the LLCP [20,33].

The identification of the locus of the dynamical crossover with the Widom line shows how relevant the connection between thermodynamics and dynamical properties is for supercooled water, and it provides strong motivation to explore further how the diffusion or relaxation time of water upon supercooling can be related to the thermodynamic properties. In this respect it is of interest to consider the empirical relations between the diffusion coefficient D and the excess entropy that have been proposed in the past. The excess entropy is defined by subtracting from the liquid entropy its ideal-gas term,

$$S_{\text{exc}} = S - S_{\text{id}} \quad (1)$$

If s_{exc} is the excess entropy per particle $s_{\text{exc}} = S_{\text{exc}}/N$, the empirical relations are based on the assumption that the diffusion coefficient is proportional to the exponential of s_{exc} [34]:

$$D \propto e^{\alpha s_{\text{exc}}/k_B}. \quad (2)$$

The right-hand side of this relation represents a measure of the distributions of the accessible configurations in the time evolution of the system. The excess entropy per particle s_{exc} can be expanded in terms of n -body terms s_n calculated by integration on the n -particle distribution functions $g^n(r_1, \dots, r_n)$ [35]. Under the assumption that the two-body term gives the main contribution in the calculations with Eq. (2), s_{exc} is approximated with the two-body excess entropy (TBEE), which can be derived from the radial distribution function $g(r)$ as follows:

$$s_2 = -2\pi\rho k_B \int \{g(r)\ln[g(r)] - [g(r) - 1]\}r^2 dr. \quad (3)$$

Different scaling relations based on Eq. (2) were formulated by Rosenfeld [34,36,37] and by Dzугutov [38]. The proposed

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scaling relations were tested by computer simulation in different liquid systems with different model potentials [34,39–46].

The behavior of the excess entropy of water was found to be connected to the structural anomaly of the liquid [46–49] and to the liquid-liquid transition [50,51]. In particular, in Ref. [46] the authors found that the Dzugutov scaled equation is in good agreement with the diffusion in supercooled water in the region of mild supercooling, where the system is in a fragile dynamical regime, while in the region of deep supercooling the Dzugutov relation starts to deviate from the simulation results.

In a previous work [23] we performed a complete analysis of the dynamical properties of the self intermediate scattering function (SISF) of TIP4P supercooled water in the thermodynamic ρ - T plane for several isochores. Along the different isochores the results agree with the prediction of MCT and in the deep supercooled region we found an FSC for densities below 1.1 g/cm^3 . According to the recent interpretation of the phenomenology of supercooled water we showed that the line of the FSC points in the ρ - T plane coincides with the Widom line.

The FSC can be interpreted in the framework of the MCT. MCT is based on the idea of the cage effect. Upon supercooling, the atoms of the liquid are trapped in the nearest-neighbor cages and they can diffuse and restore the Brownian regime when the cages relax. The time interval of the cage relaxation increases with decreasing temperature. In the asymptotic limit individuated by a temperature T_C the system enters a nonergodic regime where the dynamics is blocked. This ergodic-to-nonergodic transition upon crossing T_C is predicted by the MCT in the formulation where hopping effects are neglected; they are treated in the extended version of the theory [18]. The FSC can be considered as a crossover from a regime where hopping is negligible (fragile) to a regime where it becomes relevant (strong).

In this paper we explore the relation between the relaxation time and the TBEE in water in connection with the MCT. Importantly, we show that the TBEE has an apparent singular behavior upon approaching the asymptotic limit of the MCT crossover temperature. This is followed by a deviation from the MCT behavior of the TBEE that takes place in correspondence with the FSC calculated from the relaxation time, confirming our previous work where we found that the TBEE of TIP4P water contains signatures of low-density liquid/high-density liquid coexistence in supercooled water [51].

In Sec. II we introduce the water model and the simulation methods. In Sec. III we recall the previous results on the relaxation time in supercooled water. In Sec. IV we show how the relaxation time and the TBEE are related in water. In Sec. V the behavior of the TIP4P TBEE is interpreted in terms of the MCT and of the FSC. In Sec. VI we draw conclusions.

II. MODELS AND METHODS

The simulation of water was performed with the molecular dynamics method with the use of the TIP4P potential. The water molecule is modeled with four sites. Hydrogens (H's) are represented by two positive sites with a charge of $0.52e$ each. The H sites are connected to the neutral oxygen (O) site. The oxygen negative charge of $-1.04e$ is shifted and attributed to the fourth site (X). The OH bond length is

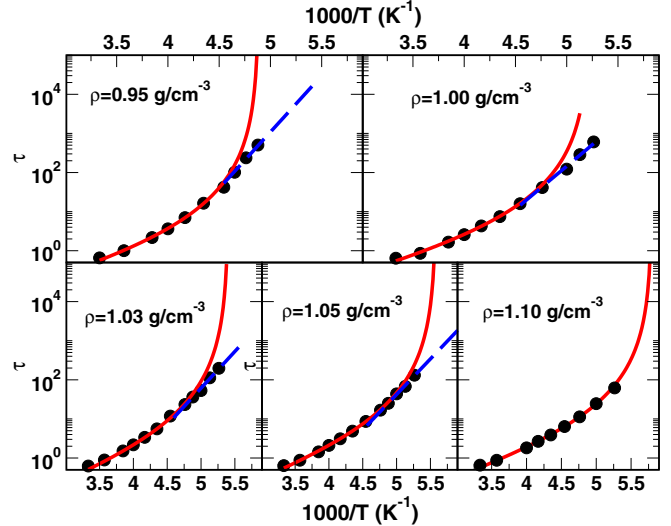


FIG. 1. (Color online) Relaxation time τ as a function of inverse temperature for different values of the density. The solid (red) curve shows the fit with the MCT power law, (4), while the dashed (blue) line is the fitting to the Arrhenius function, (5). The plots are adapted from Ref. [23].

0.9572 \AA ; the angle between the two bonds is $\theta = 104.5^\circ$. The X site lies in the molecular plane shifted 0.15 \AA from the oxygen; the OX bond forms an angle $\theta/2$ with the OH bonds. All the distances and angles are kept rigid during the simulation. Interactions between the oxygen sites of the water molecules are modeled with a the Lennard-Jones potential with the parameters $\epsilon = 0.649 \text{ kJ/mol}$ and $\sigma = 3.154 \text{ \AA}$. Charged sites are assumed to interact only with the Coulombic potential.

Periodic boundary conditions were applied and the interactions were truncated at 9 \AA . The Ewald particle mesh method was used to account for long-range electrostatic interactions. The averages of the thermodynamic and structural quantities were calculated on production runs of 30 ns starting from the equilibrated configurations of our previous work. Further details on simulation and details on calculations of the SISF functions can be found in [23].

III. DYNAMICAL CROSSOVERS IN SUPERCOOLED WATER

In a previous work [23] we calculated the SISF of the translational motion of the oxygens of the TIP4P water along various isochores from $\rho = 0.95 \text{ g/cm}^3$ to $\rho = 1.10 \text{ g/cm}^3$.

TABLE I. MCT fit parameters of τ for isochores investigated with the power law, (4), activation energies from the fit to the Arrhenius formula, (5), and FSC temperatures T_L as obtained in Ref. [23].

$\rho \text{ (g/cm}^3\text{)}$	$T_C \text{ (K)}$	γ	$E_A \text{ (kJ/mol)}$	$T_L \text{ (K)}$
0.95	204.6	2.53	55.2	224.4
1.00	191.5	2.54	42.1	217.2
1.03	185.0	2.55	36.0	210.0
1.05	179.07	2.53	34.7	200.0
1.10	172.4	2.45	—	—

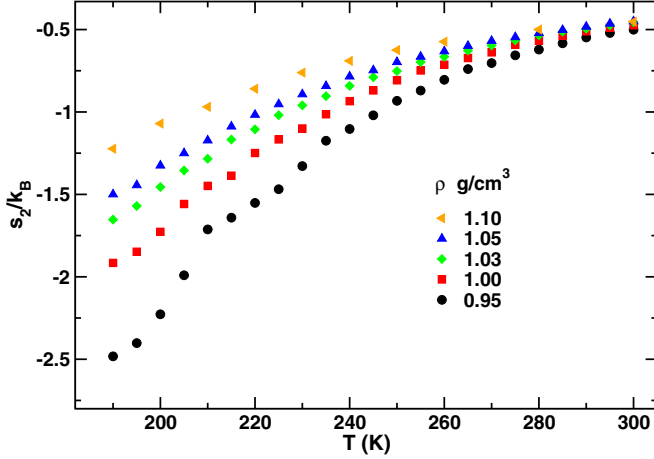


FIG. 2. (Color online) Two-body excess entropy, Eq. (3), as a function of temperature for different isochores.

The range of temperatures explored was from $T = 300$ K down to $T = 190$ K [23]. Upon cooling for each density the SISF shows the double-relaxation regime typical of supercooled liquids. At long times the SISF enters in the α -relaxation region and it decays with a behavior that can be fitted with a stretched exponential $\exp(-t/\tau)^\beta$, where τ is the structural relaxation time and β is called the Kohlrausch exponent.

In a range of temperatures of mild supercooling the relaxation time τ shows the power-law behavior predicted by MCT [18],

$$\tau = C(T - T_C)^{-\gamma}, \quad (4)$$

where C is a constant and T_C is the crossover temperature that marks the idealized transition from an ergodic to a nonergodic dynamical regime. The relaxation time and the fits with Eq. (4) as calculated in our previous work [23] are reported in Fig. 1 for different densities, from $\rho = 0.95$ g/cm³ to $\rho = 1.10$ g/cm³. It is evident that the curves for τ , apart for the highest density, deviate from the MCT prediction of

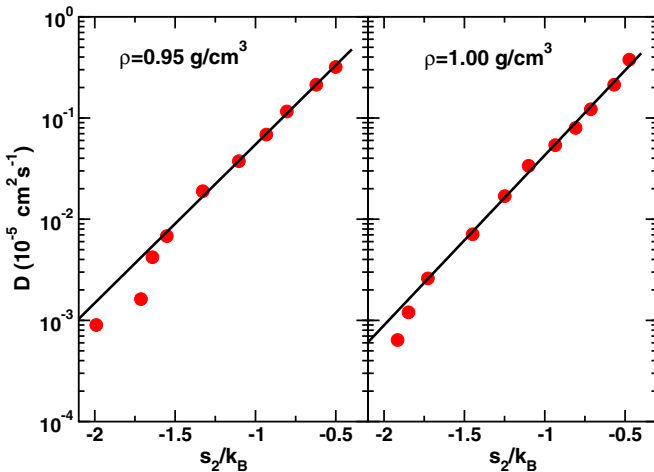


FIG. 3. (Color online) Translational diffusion coefficient D reported as a function of s_2 for the densities indicated in each panel. The solid black line is the fit to Eq. (6).

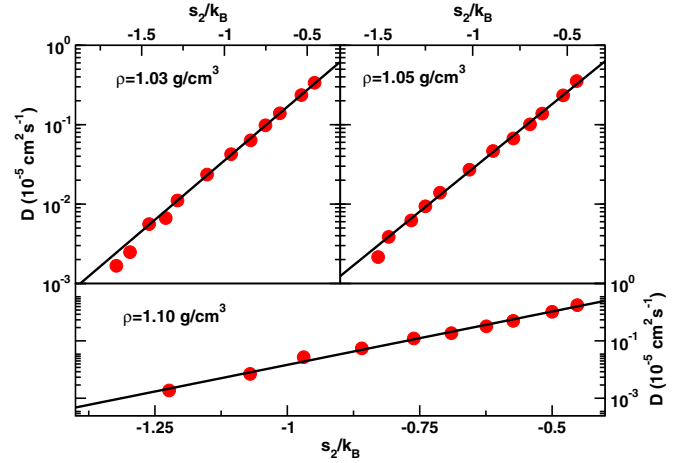


FIG. 4. (Color online) Translational diffusion coefficient D reported as a function of s_2 for the densities indicated in each panel. The solid black line is the fit to Eq. (6).

Eq. (4) at the lowest temperatures investigated, starting from a temperature $T_L > T_C$. The MCT power law, (4), marks the region of fragile behavior, and T_L marks a crossover to an exponential Arrhenius strong behavior with

$$\tau \sim \exp(E_A/k_B T), \quad (5)$$

where E_A is the activation energy.

This FSC can be explained in terms of hopping effects. Before the asymptotic limit T_C is reached, hopping effects neglected in the ideal version of MCT intervene and restore ergodicity, inducing a change in the behavior of τ at decreasing temperature below T_L . This finding is in agreement with the FSC found in other models of water [20,21,25].

For the highest density investigated, 1.10 g/cm³, we can fit the curve with Eq. (4) for the entire range of temperatures explored in our simulations. The relation between the FSC and the presence of a LLCP in water has been discussed in the previous work and this behavior, connected with the fact that the 1.10 g/cm³ isochore does not cross the Widom line, has been interpreted in detail there. We list in Table I the results obtained with the fits shown in Fig. 1.

IV. TWO-BODY ENTROPY, DIFFUSION, AND RELAXATION TIME

Now we explore the connection of the excess entropy with the diffusion and the relaxation time in our system. Since in this work we are interested in the translational dynamics of pure

TABLE II. Fit parameters of D vs s_2 according to Eq. (6).

ρ (g/cm ³)	A_D (10 ⁻⁵ cm ² s ⁻¹)	α_D
0.95	2.020	3.61
1.00	2.047	3.87
1.03	2.122	4.09
1.05	2.399	4.45
1.10	2.969	5.19

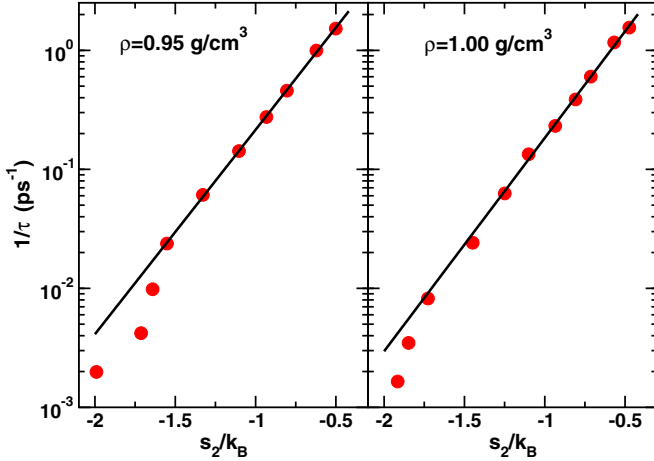


FIG. 5. (Color online) Inverse of the α -relaxation time reported as a function of s_2 for the densities indicated in each panel. The solid black line is the fit to Eq. (7).

water, s_2 is derived from the oxygen-oxygen radial distribution function and in (3) we identify $g(r)$ as $g_{OO}(r)$.

In Fig. 2 we report s_2 , as extracted from the $g_{OO}(r)$ of our simulations [52], as a function of temperature for different isochores. The excess entropy gives a negative contribution whose modulus increases with decreasing temperature. While the slope is monotonous for all isochores, changes in the curvature are present, which are more evident for the lower densities. Their meaning is discussed later.

As stated in Sec. I, Eq. (2) hypothesizes a relation between the diffusion coefficient D and an exponential of the excess entropy that can be written as

$$D = A_D e^{\alpha_D s_2 / k_B}, \quad (6)$$

with $A_D = A_D(\rho)$ and $\alpha_D = \alpha_D(\rho)$. We report in Fig. 3 D as a function of s_2 for the densities 0.95–1.00 g/cm³ and in Fig. 4 that for higher densities, 1.03–1.10 g/cm³, and the fits to Eq. (6). The fitting parameters are listed in Table II. We comment below on the results obtained.

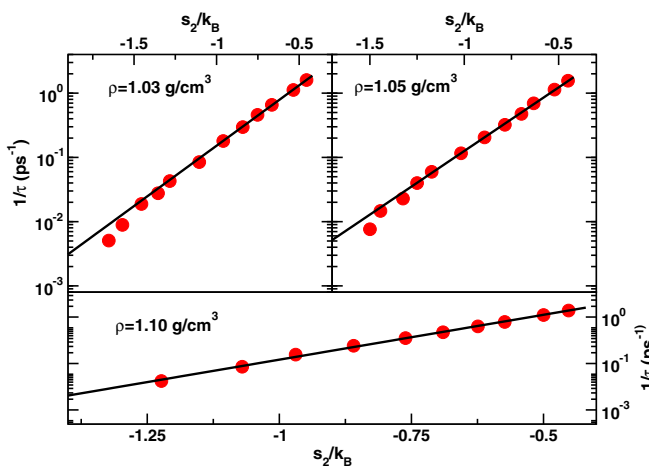


FIG. 6. (Color online) Inverse of the α -relaxation time reported as a function of s_2 for the densities indicated in each panel. The solid black line is the fit to Eq. (7).

TABLE III. Fit parameters of $1/\tau$ vs s_2 according to Eq. (7). T_{\min} is the approximate lower temperature at which the fit can be applied. T_L is the FSC crossover temperature as obtained in Ref. [23].

ρ (g/cm ³)	A_τ (ps ⁻¹)	α_τ	T_{\min} (K)	T_L (K)
0.95	11.23	3.95	220.0	224.4
1.00	11.39	4.13	210.0	217.2
1.03	11.51	4.32	200.0	210.0
1.05	11.98	4.56	195.0	200.0
1.10	20.90	5.79	—	—

With the idea that the relaxation of a supercooled liquid is determined through the cage effect by the accessible configurations, we assume that an analogous relation is valid also for the relaxation time,

$$\frac{1}{\tau} = A_\tau e^{\alpha_\tau s_2 / k_B}, \quad (7)$$

with $A_\tau = A_\tau(\rho)$ and $\alpha_\tau = \alpha_\tau(\rho)$, as before. It is particularly important to study the behavior of τ , which is a more significant parameter for MCT test than D . In fact, D can show more marked deviations from the predicted MCT behavior upon approaching T_C . This was observed in MCT analysis of different glass-forming liquids; see, for example, Refs. [53] and [54].

We check whether this relation between τ and the excess entropy is satisfied by plotting τ^{-1} as a function of s_2 and by fitting the curves with Eq. (7). The results are shown in Fig. 5 for the densities 0.95–1.00 g/cm³ and in Fig. 6 for higher densities, 1.03–1.10 g/cm³. The fitting parameters are listed in Table III.

It is clear that the fits both to Eq. (6) for D and to Eq. (7) for τ are accurate in a range that excludes the lower temperature values apart from the case 1.10 g/cm³. To connect with the results shown in the previous section we consider, in particular, the plots of τ in Figs. 5 and 6 and the deviations from

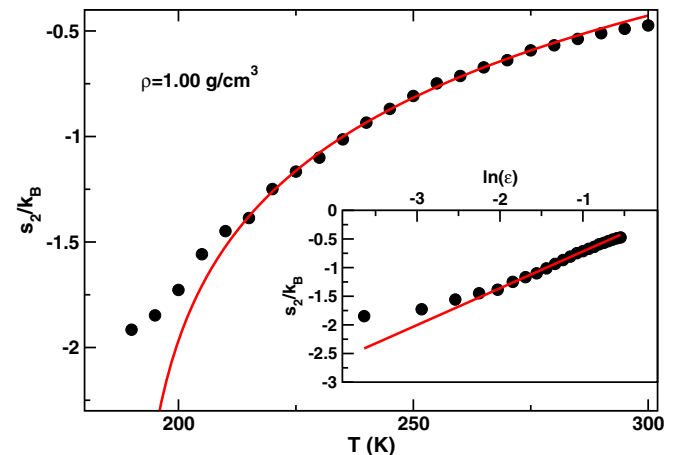


FIG. 7. (Color online) Two-body excess entropy as a function of T for $\rho = 1.00$ g/cm³ (black circles). The fit in the fragile region [solid (red) line] was done with Eq. (8). Inset: The same functions are reported as a function of $\ln(\epsilon)$.

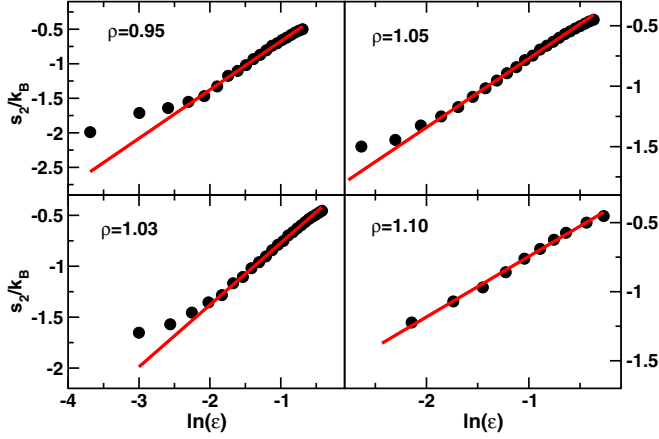


FIG. 8. (Color online) Two-body excess entropy as a function of $\ln(\epsilon)$ (black circles) fitted in the fragile region with Eq. (8) [solid (red) line]. The density is indicated in each panel.

exponential behavior. The estimated lowest temperature T_{\min} for which Eq. (7) can be applied are listed in Table III.

By considering the previous results for the α -relaxation times reported in Fig. 1 we observe that the temperature T_L at which the FSC was found for each density [23] is very close to T_{\min} , as also shown in Table III. For the density $\rho = 1.10 \text{ g/cm}^3$ the FSC is not found, and correspondingly the fit of τ with Eq. (7) is valid over the whole temperature range explored in our simulation. Returning to Fig. 2 we now note that the change in curvature of s_2 at low temperatures for all the isochores, except $\rho = 1.10 \text{ g/cm}^3$, corresponds to the FSC.

Importantly, from our findings it can be deduced that the exponential relation, Eq. (7), that we hypothesized between τ and s_2 is certainly valid for TIP4P water but only in the fragile regime where MCT holds [23]. Deviations appear when the system crosses the FSC, which, in water, also coincides with the Widom line.

V. ASYMPTOTIC BEHAVIOR OF THE TWO-BODY ENTROPY AND MCT

As stated above, in the fragility range the α -relaxation time follows the asymptotic behavior predicted by MCT, Eq. (4). Now if we take into account the exponential form, (7), of $1/\tau$ as a function of s_2 , an asymptotic behavior for the TBEE can be predicted.

TABLE IV. Fit parameters of Eq. (8) and the resulting T_C compared with the MCT crossover temperatures [23]. The values of γ obtained from Eq. (10) are also reported.

$\rho \text{ (g/cm}^3\text{)}$	B	b	$T_C \text{ (K)}$		γ	
			From Eq. (8)	From MCT [23]	From Eq. (10)	From MCT [23]
0.95	0.02754	0.7024	200.0	204.6	2.77	2.53
1.00	-0.07584	0.6423	190.0	191.5	2.65	2.54
1.03	-0.1627	0.6085	181.0	185.0	2.63	2.55
1.05	-0.2001	0.5701	177.3	179.07	2.60	2.53
1.10	-0.3062	0.4382	170.1	172.4	2.54	2.45

In terms of the reduced temperature $\epsilon = (T - T_C)/T_C$, formula (7) can be written as

$$s_2/k_B = B + b \ln(\epsilon), \quad (8)$$

where

$$B = -\frac{1}{\alpha_\tau} \ln\left(\frac{CA_\tau}{T_C^\gamma}\right), \quad (9)$$

with C and A the coefficients of Eqs. (4) and (7), respectively, and

$$b = \frac{\gamma}{\alpha_\tau}. \quad (10)$$

In Fig. 7 the fit of s_2 as a function of T obtained with Eq. (8) is reported for the density 1.00 g/cm^3 . We can clearly see that this formula applies only in the fragile range. In the inset the two-body entropy is reported as a function of $\ln(\epsilon)$ to make more evident the linear behavior and the deviation from it.

The same kind of fit can be performed for the other densities and the results are shown in Fig. 8. In Table IV we list the fitting parameters. We also report the values of the exponent γ obtained from definition (10). It is particularly relevant to observe that both the asymptotic crossover MCT temperatures obtained in these fits and the γ values extracted from Eq. (10) are very close to the values that come from the MCT analysis of the dynamics performed in Ref. [23].

Therefore the two-body entropy shows a nonanalytic behavior at the MCT crossover with an apparent asymptotic logarithmic divergence. As hopping intervenes to restore ergodicity, Eqs. (7) and (8) no longer hold.

VI. CONCLUSIONS

Study of the interplay between the thermodynamic and the dynamic properties of a liquid is essential for the theoretical interpretation of many phenomena. This issue is of particular relevance in the case of supercooled water, where there is still a vivid debate about water anomalies.

In our work we have shown that the TBEE of supercooled water is strictly related to the diffusion coefficient D and the relaxation time τ . This is in agreement with a previous analysis of the diffusivity in the fragile region of supercooled water [46]. Our use of Eq. (7) for τ is based on the idea that the relaxation processes of the liquid are related to the number of available configurations.

Importantly we connect the validity of relation (7) to the recent phenomenology of supercooled water. We find in fact that Eq. (7) is verified in the range where the MCT is valid

and the hopping processes can be neglected. The deviation of the data from Eq. (7) marks the FSC behavior of liquid water, where the Widom line of the liquid-liquid critical phenomenon is also located. We would like to stress that while the FSC is a rather general feature of formerly liquid glass, the fact that it happens upon crossing a thermodynamic locus connected to a critical point, the Widom line, is only related to supercooled water, which, at least for this class of potential, shows an LLCPC in the vicinity of the FSC line.

The approximation of s_{exc} with s_2 gives a good description of the behavior of the diffusion coefficient in supercooled water at least in the fragile region, as already found for the diffusion coefficient [46]. We have found now that the TBEE shows a logarithmic divergence at the MCT crossover temperature T_C . It appears that the TBEE, a rather easy function to calculate from the radial distribution function, can be considered a useful marker of the MCT crossover. In the interpretation of this result

it must be considered that MCT equations contain as input the two-body structure of the liquid. Moreover, the TBEE has the MCT properties only when hopping can be neglected, and this indicates that the presence of hopping influences the TBEE.

It would be of interest in the future also to explore s_{exc} in the region of hopping and the systematic corrections due to n -body terms. The contribution to the entropy of higher structural correlations and its relevance have recently been discussed for glass forming liquid models [55].

Our results indicate important connections between relaxation time and entropy that merit further exploration in future, and not just for supercooled water.

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